The Application of the "Reaction Order Approach" to a Complex Electrode Mechanism. Pitfalls in Drastic Media Changes

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Amatore, Pinson and Savéant [1] have recently attempted to discredit the so-called "reaction order approach" developed in this laboratory [2] for the analysis of electrode mechanisms. The approach was developed especially for complex reaction schemes for which theoretical data are not available and involves the determination of the apparent rate law for a process without carrying out any calculations. However, Amatore, Pinson and Savéant claim that the approach only works for simple reactions and fails when the rate is determined by more than a single step.[1] It is the purpose of this communication to demonstrate that this is not the case.

More recently, Amatore, Pinson and Savéant [3] have published another note dealing with the anion radical–proton donor complex mechanism for the dimerization of anion radicals. This mechanism was observed during the electrodimerization of diethyl fumarate anion radical in DMF and can be described by eqns. (1) and (2).[4]

$$A^{\cdot-} + H_2O \overset{K_1}{\rightleftarrows} A^{\cdot-}/H_2O \tag{1}$$

$$A^{\cdot-}/H_2O + A^{\cdot-} \xrightarrow{k_2} A_2^{2-}/H_2O \tag{2}$$

Amatore, Pinson and Savéant apply this mechanism to the dimerization of 9-cyanoanthracene anion radical and attempt to direct the mechanism to reaction (3) as the rate determining step by going to very high (16 M) water concentrations.[3]

$$2\ A^{\cdot-}/H_2O \xrightarrow{k_3} A_2^{2-}/2\ H_2O \tag{3}$$

A non-linear dependence of the apparent rate constant on $[H_2O]$ was observed and interpreted in terms of a significant contribution of (3). Although this is an expected consequence of going to very high water concentrations, the data are inconclusive because there could be a large effect of the change of the medium from essentially aprotic to 16 M water.

The rate laws for the two cases with different rate determining steps are (4) and (5).

$$\text{Rate} = k_2K_1[A^{\cdot-}]^2[H_2O] \tag{4}$$

$$\text{Rate} = k_3K_1^2[A^{\cdot-}]^2[H_2O]^2 \tag{5}$$

A deuterium equilibrium isotope effect was observed earlier for rate law (4).[4] The fact that the exponent of K_1 differs in the two rate laws suggests a possible way to verify the occurrence of reaction (3). At low $[H_2O]$, only rate law (4) is expected to apply when K_1 is small as it is when $A^{\cdot-}$ is $ANCN^{\cdot-}$. The apparent deuterium isotope effect for this case would be that for equilibrium (1). Under conditions where rate law (5) is significant, the apparent isotope effect should reflect the contribution from K_1^2 and should be either greater or less than that at low $[H_2O]$ depending upon whether $(K_1)_H/(K_1)_D$ is greater or less than unity.

In order to test for a dependence of the apparent kinetic isotope effect on $[H_2O]$, experiments were carried out in both dimethylsulfoxide (DMSO) and dimethylformamide (DMF) in which the water (or deuterium oxide) concentration was varied from 1 to 16 M. Over the entire range in DMSO and up to 14 M (H_2O) in DMF the values of $(k_H/k_D)_{app}$ were observed to be independent of $[H_2O]$ and equal to 1.07±0.07 (DMSO) and 0.87±0.03 (DMF). At the highest water concentration (16 M) $(k_H/k_D)_{app}$ in DMF changed from less than one to 1.1. Aside from the questionable change in the last case there did not appear to be any significant contribution from rate law (3).

In order to test for a possible substrate concentration effect on $(k_H/k_D)_{app}$ [ANCN] was varied from 0.125 to 1.00 mM in both solvents 16 M in H_2O (or D_2O). The apparent kinetic isotope effects were independent of substrate concentration (Table 1) within experimental error. However, the data are most revealing. The fourth column gives the "reaction order approach" criterion for a reaction second order in anion radical, *i.e.* v_c/[ANCN] is required to be constant to be consistent with either rate law (4) or (5).[2] The latter varies by a factor of almost 4 in both solvents. Thus, the "reaction order approach" rules out either rate law under the conditions of the experiments. Furthermore v_c is essentially constant in both solvents at [ANCN] of 0.5 to 1.00 mM. This means that $R_{A/B}$ which is the sum of the reaction orders in ANCN and $ANCN^{\cdot-}$ is equal to 1 in this concentration range.

But what was the basis for the proposal by Amatore, Pinson and Savéant [3] that rate laws (4)

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Table 1. Reaction order and deuterium kinetic isotope effect analysis of the reactions of 9-cyanoanthracene anion radical in aqueous DMF and DMSO.[a]

[ANCN]/mM	Solvent	v_c/V s^{-1} [b]	v_c/[ANCN]	k_H/k_D
0.125	DMF	125.8	1006	1.18
0.250	DMF	184.4	738	1.19
0.375	DMF	240.0	640	1.19
0.500	DMF	264.1	528	1.08
0.750	DMF	272.7	364	1.16
1.000	DMF	253.6	254	1.10
				1.15(0.05)
0.125	DMSO	64.6	517	0.89
0.250	DMSO	116.1	464	1.19
0.500	DMSO	166.1	322	1.01
0.750	DMSO	171.7	229	1.00
1.000	DMSO	166.0	166	1.03
				1.02(0.11)

[a] In solvent containing H_2O or D_2O (16 M) at 293.4 K. [b] The subscript c indicates that v was evaluated at a constant value of the derivative peak ratio; 0.500 in DMF and 0.400 in DMSO.

Table 2. Linear sweep voltammetry data for the reduction of 9-cyanoanthracene in aqueous dimethylsulfoxide.[a]

$[H_2O]$/M	Electrode	dE^p/d log v [b]	$-$dE^p/d log C_A [c]
1.39	Au	13.5 (0.5)	16.3 (200)
1.39	Au	17.0 (1.0)	13.3 (400)
1.39	Au	18.1 (2.0)	7.6 (1000)
2.78	Au	16.9 (0.5)	15.4 (200)
2.78	Au	17.2 (1.0)	14.3 (400)
2.78	Au	19.8 (2.0)	12.1 (1000)
8.33	Hg	19.6 (0.5)	11.0 (200)
8.33	Hg	20.4 (1.0)	11.8 (400)
8.33	Hg	19.7 (2.0)	11.0 (1000)
13.9	Hg	20.1 (0.5)	11.2 (200)
13.9	Hg	20.1 (1.0)	12.0 (400)
13.9	Hg	21.6 (2.0)	9.8 (1000)
13.9	Au	20.4 (0.5)	12.3 (200)
13.9	Au	20.7 (1.0)	12.3 (400)
13.9	Au	22.3 (2.0)	10.1 (1000)

[a] In solvent containing Bu_4NBF_4 (0.1 M) at 18.8 °C. [b] In mV/decade. The number in parentheses refers to the substrate concentration. [c] In mV/decade. The numbers in parentheses refer to v.

and (5) describe the reactions of $ANCN^{\cdot-}$ in aqueous DMSO? They apparently only studied the kinetics at a *single* concentration, *i.e.* 1.0 mM. They make the following statement: " Linear sweep voltammetric peak shift at low sweep rates (*i.e.*, in conditions where the reduction wave is chemically irreversible) with ANCN concentration and sweep rate (19 mV per log unit at 20 °C) indicate the occurrence of a radical–radical coupling dimerization process in the whole water concentration range (0–16 M)". This statement is difficult to understand in view of the fact that the reduction wave is chemically reversible at low sweep rates in dry solvents (see

Table 2 of Ref. 5) and it was not possible to get meaningful linear sweep voltammetry (LSV) results in DMF for this reason. Thus, it was necessary to re-investigate the LSV behaviour of ANCN in aqueous DMSO (Table 2). At the lowest $[H_2O]$, 1.39 M, the data resemble that observed in dry DMF.[5] The value of $dE^p/d \log v$ was observed to be dependent upon [ANCN] and $dE^p/d \log C_A$ was dependent upon v. At $[H_2O]$ greater than 2.78 M, $dE^p/d \log v$ was close to the value expected for second order dimerization, *i.e.* 19.3 mV/decade at 291.9 K, but in all cases $dE^p/d \log C_A$ was considerably lower than the theoretical value. Obviously, at high water concentrations the LSV data are not consistent with the dimerization mechanism and indicate either competing reactions or a complex rate law.

Both derivative cyclic voltammetry reaction order analysis and the LSV data indicate that there is a mechanism change in going from low to high water concentration in DMSO during the reduction of ANCN. In order to determine just what the mechanism is would require further experimental work. In the opinion of the author, the effort is not warranted. The complication of the change in mechanism was brought about by studying the reaction under very unusual conditions, in aprotic solvents containing up to 16 M H_2O. The reactions are much more well-defined in dry solvents.

This work shows that the "reaction order approach" can give valuable information when applied to complex reactions. In this case it reveals a complex kinetic pattern which is inconsistent with the previous mechanism proposal.[3] This work also points out the pitfalls in attempting to extend mechanisms from aprotic solvents to highly aqueous systems. It is apparent that it is not safe to assume that the reaction orders and the mechanism of a reaction remain the same when drastic changes are made in the reaction conditions.

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